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学 位 論 文 [博 士 (工 学)]

Electrochemical study of FcMA- immobilized mono-dispersed polystyrene particles

(フェロセンアクリル酸エステル固定化単分散
ポリスチレン粒子の合成と電極過程)

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Content

Abstract I

Chapter 1

Introduction

1.1 Colloid 1
1.2 Polymer colloids-latex 1
1.3 The synthetic methods 3
1.4 Composite latex particle 3
1.5 Characterization methods 4
1.6 Model of latex particles 5
1.7 Electrochemistry of latex particles 6
1.7.1 Surface-charged latex particles 6
1.7.2 Conductive polymer coated latex particle 6
1.7.3 Ferrocene immobilized latex particles 6
1.8 The aim of thesis 8
1.9 References 10

Chapter 2

Preparation and electrochemical characterization of ferrocenyl-coated polystyrene monodispersed latex particle

2.1. Introduction 15
2.2. Experimental 16
2.2.1. Materials 16
2.2.2 Synthesis of monomer FcMA 16
2.2.3. Synthesis of ferrocenylmethanol acrylate coated PS latex 17
2.2.4. Electrochemical measurements and instrumentations 17
2.2.5. Aanalysis of size, size-distribution and particle-dispersion 17
2.2.6. Analysis of chemical composition 17
2.3 Result and discussion 18
2.3.1 Determination of particle size, uniformity and stability 18
2.3.2 Copolymerization 19
2.3.3 Characterization of chemical composition 19

2.3.4 Electrochemical behavior of FcMA-PS particle 21
2.4 Summary 23
2.5 References 25

Chapter 3

The impact of particle size on electrochemical activity by ferrocenyl-immobilized polystyrene latex particles

3.1 Introduction 26
3.2 Experimental 27
3.2.1.Chemicals 27
3.2.2 Synthesis of ferrocenylmethanol acrylate (FcMA) 28
3.2.3 Synthesis of FcMA / styrene copolymer 29
3.2.4. Synthesis of ferrocenylmethanol acrylate coated PS latex 29
3.2.5. Measurements and instrumentations 31
3.3 Result and discussion 31
3.3.1 Properties of FcMA-PS latex 31
3.3.2 Voltammetry of FcMA-PS suspensions 36
3.4 Surmmary 39
3.5 References 40

Chapter 4

Conclusion

Conclusion 42
Acknowledgement 44

Abstract

Ferrocenylmethanol acrylate (FcMA)-immobilized polystyrene (PS) latex particles (FcMA-PS) were synthesized via the emulsion copolymerization of FcMA and styrene on the surface of PS latex seed in diameter 0.9μm. Comparing them with parental PS particles, the morphology of FcMA-PS particle and size were not changed clearly. They were almost spherical, uniform, mono-dispersed and stable in aqueous suspension as demonstrated by an optical microscope, scan electromicroscope (SEM) and light scattering instrument. The FcMA-PS latex particles in aqueous suspension showed a couple of stable voltammetric waves at 0.271/ 0.207 V vs Ag | AgCl, potential difference was 0.064V. The redox reaction on electrode came from the ferrocene moieties of FcMA-PS latex rather than the FcMA molecule or oligomer in suspension, because no any redox peak could be found in CV of supernatant obtained by centrifugation of FcMA-PS suspension.The anodic and cathodic peak current of FcMA-PS in aqueous suspension were proportional to square root of scan rate. Electrode reaction process of latex was controlled by diffusion of particles to electrode, as if it were huge redox molecules. However, when we compared the redox unit numbers determined by cyclic voltammogram (n_{CV}) and UV spectrum (n_{UV}), we found that only a part of redox unit took part in electrode reaction. In other word, the electrode reaction of FcMA-PS latex particle was partial charge transferred. The partial charge transfer may be ascribed the thickness.of double electrical layer is less than the diameter of particle. And more reasonable interpretation may be obtained by an investigation of the voltammetric behavior of various sized FcMA-PS latex.

Various sized FcMA-PS latex particle were synthesized with aboved method in terms of different sized polystyrene latex seed at the aim of investigating the size-effect of particles on the electrochemical activity of FcMA-PS latex particle. FcMA-PS latex particles in present work rang diameters from 0.084 to 1.7 μm. The amounts of the ferrocenyl moiety loaded on one particle were proportional to the radii, *a*. The

proportionality suggests the uniform distribution of the ferrocenyl moiety over the particle rather than forming a core-shell latex, of which common concentration was 0.18 M. The aqueous suspensions, which were stable in the presence of a surfactant, exhibited reversible voltammetric waves for the ferrocenyl moiety. The peak current was controlled by diffusion of the latex particles. The efficiency of the reaction was obtained from the ratio of the observed current to the theoretical one which was estimated from the number of the ferrocenyl moieties and the diffusion coefficient of the particle by the Stokes-Einstein relation. The ratio was proportional to $a^{-0.47}$, whereas it might be a^{0} for an ideal particle without any size effect. This relation was explained in terms of the contribution of rotational diffusion of redox particles rather than the thickness of double electrical layer is less than the diameter of particle.

Keyword : *Ferrocenylmethanol acrylate(FcMA), Polystyrene(PS) , Latex, Suspension, Diffusion, Size-effect, Cyclic voltammetric, Diffusion-controlled, Partial charge transfer*

Chapter 1

Introduction

1.1 colloid

Colloids and colloidal suspensions are dispersions of small particles, ranging in size from one nanometer to one micrometer, in supporting substance (liquid, gas, gel, etc). These particles are different from solute in that, they can not diffuse through a semipermeable membrane. The concept of colloids was introduced in 1861 by Scottish scientist Thomas Graham[1]. Butter, milk, cream, aerosols (fog, smog, smoke), asphalt, ink, paint, glues, and sea foam can be regarded as colloids.

Brownian motion is the random collision to the particles by the solvent molecules. This prevents the colloid particles from sedimentation out of the solvent. More importantly, Brownian motion contributes to the diffusion of particles in solvent. In 1905, Albert Einstein investigate this phenomena and derived a general equation for the diffusivity of colloidal particles in solvent.

1.2 polymer colloids----latex

As a kind of colloids, latex is defined as “a colloidal dispersion of polymer particles in a medium” (usually in water) by Union for Pure and Applied Chemistry [2]. With the development of polymerization technology, the latex dispersion have been prepared by various polymeric methods and used in bio-related field [3,4,5,6], paints, adhesives, ink, cosmetics, paper making, medical science and model system of atoms or molecule [7,8,9,10]. The extensive application of latex particles is due to water-based system avoid environmental problems associated with organic solvent based systems and development of numerous synthetic methods.

In generally, latex particles provide small size and large surface areas, the diameter of latex particles range from 10nm to some micrometers, it can be regarded as spots indicating the existing positions [11]. For example, the total surface area of 1g of latex particles with diameter of 0.1μm is about $60m^2$. This surface area is available for the sites of adsorption and desorption, chemicals reaction, light scattering, etc. Latex particle in

suspension has a lower viscosity and higher fluidity compared to solutions containing the same amount of solid [12]. Latex particles in suspension can move through the medium by gravity, electric fields via Brownian motion. These movement keep a fresh interface between the particles and medium. Such particle sometimes exhibit a fairly high electrophoretic mobility even if they have little charge. This is the reason for extraordinarily high electrophoretic mobility of cell [13]. The movement of the particles enable us to make a real time observations of motion of particles, which have been impossible for atomic and molecular systems. Thus polymer colloids are realistic model for atoms and molecules. The most important character of latex is the stability of its dispersion. The potential energy of latex particle in suspension and consequently the stability of the latex itself are determined by the contribution of three factors: electrostatic repulsive force, Van der waals's attractive forces and steric repulsive forces among the particles. The classic colloid stability theory of - DLVO theory (Derjaguin–Landau [14] -Verwey-Overbeek [15]) - includes the first two force. If the particle has a high potential energy , it has a high stability ratio W and is stable enough to be stored for a relatively long period, for instance, more than one month or more longer [16] . (Herein, stability ratio W is given by: W = Kq / Ks, Kq and Ks are the rate constant for rapid and slow flocculation, respectively.). The surface potential energy is affected significantly by environmental factors such as ionic strength and pH value. The minimum concentration of a salt to flocculate the particles is termed the critical flocculation concentration (CFC) [17]. Steric repulsive interactions are crucial force for latex particles covered with a surfactant layer in suspension. The steric stabilization effect consists of both an enthapy and entropy effect. The overlap of the surface layers of two vicinal particle results in a shift from the equilibrium state of the layer(i.e. entropy gain) and in a decrease in the conformational freedom of solvated polymer chains (i.e. entropy loss) [18]. The critical temperature for flocculation is called the critical flocculation temperature (CFT). The high stabilities of latex suspension may make it difficult to separate micro-spheres from the dispersion medium. High-speed and low-temperature centrifugation, salt sedimentation, filtration etc [19,20] are main methods to separate latex particles from dispersion. The uniformity is a paramount feature and is the basic requirement for such as carriers in antibody diagnostic tests and model system for simulation of colloidal nucleation, crystallization . [21,22,23,24], Herein, Monodispersity usually refers to a ratio of Weight-average diameter to Number-average diameter is less than 1.005 [25].

1.3 The synthetic methods

The most important method for preparing latex is emulsion polymerization [26,27,28], which has been extensively reviewed by Ugelstad et al [29]. Size, surface charge density and types of function group can be controlled by varying the conditions of polymerization. Since the conditions are flexible and cover requirements for synthesizing various micro-spheres. In the synthetic processes, multiple nucleation, random coagulation, impurities and inhibitors should be avoided [30]. Others synthetic methods including soap-free emulsion polymerization [31,32], dispersion polymerization [33], precipitate on polymerization [34], suspension polymerization [35], micro-emulsion or mini-emulsion polymerization [36,37] The size distribution of latex particles and dispersion medium in these methods was shown in Fig1.1.

In order to prepare the core-shell structure composite latex particle, enlarge the particle size or introduce new functions into latex particles, we have used seeded polymerization which was developed by Ugelstad [38] . The main processes of the seeded polymerization are preparation of latex seed and polymerization or chemical graft of the monomer. A review on the formation of composite particle by seeded polymerization was also given by Tubokawa [39]. The seeded polymerization processes are sometimes accompanied penetration of monomer into latex instead of forming the shell on latex surface [40]. Donald Sundberg have been studied the penetration rate of monomer into PS and PMMA seed latex particles [41].

1.4 Composite latex particle

There is a considerable interest in preparation of composite latex particles by adding second materials to primitive particles through seed polymerization, co-precipitation and chemical connection. Such composite latex being thought to form core shell structure, shows interesting optical, electrical, surface chemical and catalytic properties. For example, the magnetic Fe_3O_4 was introduced on latex surface or inner to obtain the magnetic latex [42]; the silver or gold nanoparticles were immobilized on the latex surface to obtain the metallic latex particles [43]; hemine–coated core-shell polystyrene latex showed the catalytic activities on the oxygen and carbon dioxide [44]. In these composite latex series, core play a role in keeping a given geometry and size, shell provide particles such function as hydrophobicity / hydrophilicity, chemical

activities, charge-charge interaction. An advantage of core-shell particles lies in simple modification of the shell to exhibit functionalities. For example, shells are tailored to keep the core dispersed in a solvent and are applied to protecting the core of medicines from dissolution or hydrolysis [45]. The core-shell particles with different glass transition temperatures can be used to modify the mechanical properties of thermoplastic [46,47] and to manufacture polymeric nano-composite materials with a periodic structure [48].

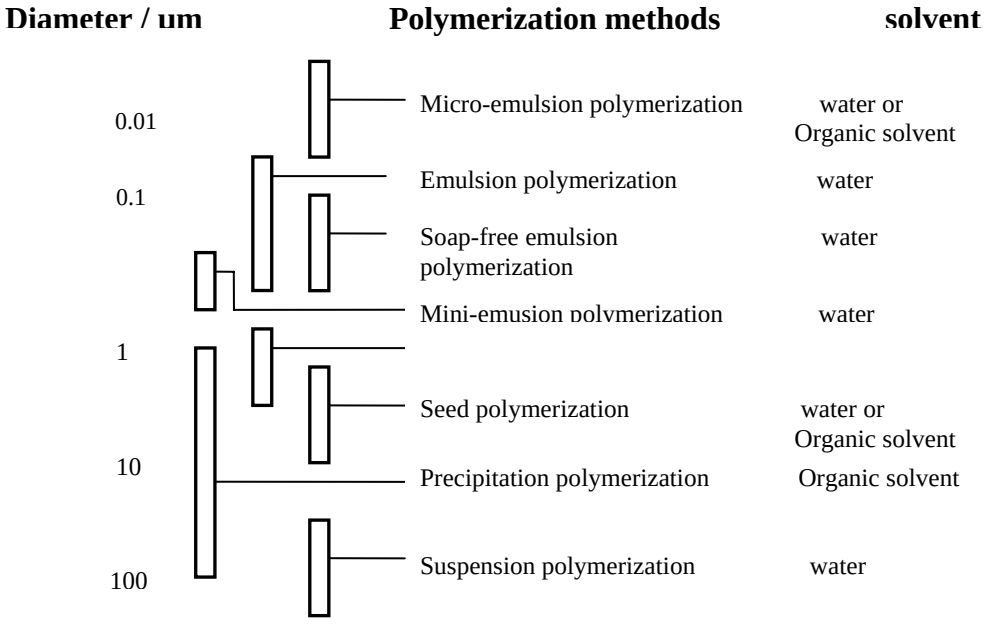

Fig1.1.The synthesis methods of latex particles and corresponding diameter and solvent

1.5.Characterization methods

There are many techniques of characterizing colloidal latex particles. The particle size and its distribution has usually been measured by dynamic light scattering (DLS), capillary hydrodynamic fraction (CHDF). Morphology can be determined by scanning electron microscope (SEM), atomic force microscope (AFM), transmission electron microscope (TEM). surface composition usually characterized by FT-IR, NMR, UV. If latex is composed of two components, especially for core-shell latex particle, it can been identified by solvent extraction technique. The example core of polyaniline coated polystyrene latex can be extracted by tetrahydrofuran (THF) to give a ‘broken-egg-shell’

polyaniline shell [49], Another effective method is to dye one component with OsO_4, RuO_4 or CH_3I [50] to identify core- shell structure in existence.

1.6 Model of latex particles

About fifty years ago, Lawrence Bragg and J.F.Nye devised a scheme for making a model of metal crystals [51]. Their so-called bubble rafts visualized successfully grain boundaries, point defects, dislocations, recrystallization, and annealing. However one serious disadvantage was poor reproducibility by thermal motion of bubble rafts. When latex particles are dispersed into a liquid, their behavior can be seen under optical microscope with the technique developed by Hachisu et al [52]. When the refractive index difference between the liquid and the particles is large enough , the long time scale of the motion of latex particles enables us to make real time observation. Thus the polymer latex dispersion can be expected to be a more realistic model for atoms and molecules than the bubble rafts. For example, Marina de Moraes Lessa utilized hetero-flocculation of amidine polystyrene latex and anticarsia gemmatalis nucleopolyhedrovirus as a model system for studying sunlight protection [53]; A. Brindley used polystyrene colloids with surface-grafted polyethylene oxide as model systems for site-specific drug delivery [54]; Comper used latex dispersion as a model system to study the cell transport mechanism[55]; Aoki ,et al used ferrocene immobilized polystyrene latex to evaluate the diffusion-controlled electrode reaction models of redox latex particles, there are three kind of models as (a) the reaction only occured in the geometrical domain; (b) a given thickness of reaction layer from the electrode; (c) a rotational diffusion of particle to electrode. Asher et al developed a thermal switch system by means of themo-sensitive polyisopropylacrylamide polymer colloid [56]; Pierre Michaïlesco provided a possible route to model endodontic bacterial leakage by calibrating latex spheres percolation [57]; Thomas Palberg used combined Bragg and small angle light scattering and of charged sphere to give out crystallization kinetics of repulsive colloidal spheres. Because latex are size-controllable materials, it has often played a significant role in size effect, Li et al studied the effect of PS particle size on the adsorption amounts of copolymer, and observed that the layer thickness of copolymer on latex surface increased with the PS latex size [58,59]. The dependence of the current of ferrocene immobilized PS latex with the diameter of the particles, etc [60].

1.7 Electrochemistry of latex particles

The electrochemical study of large particles with multi-redox center such as fullerene [61], metal nanoparticles [62] and redox dendrimers[63] have attracted a considerable interest in the electrochemical field. These large particles can act as potential candidates for the multielectron redox catalysts and serve as model for the studies of light –initiated intramolecular electron transfer [64]. As a member of large particle family, redox-active, monodispersed, spherical, wide-size-range latex particle is a good substance for electrochemical study, because it can realize immobilization of more redox sites on one particle and visualize the electrode reaction behavior by microscope.

1.7.1 Surface-charged latex particles

The surface-charged latex particle has been utilized as a model to investigate interaction among particles as well as between particles and their counterions [65,66].The sulfonate latex particles in salt-rich suspension show the behavior of strong acid, whereas those in well-deinonized suspension show a weak acid [67]. The increase in pH with a decrease in concentration of supporting electrolyte has been proved not only by the decrease in reduction current of H+ in the latex suspension [68] but also by the conductivity of latex suspension [69,70]. Well-deionized suspension of sulfonated PS can exhibit iridescence, because order structure of particles [71,72,73,74] is formed by electrostatic interaction between neighboring charged particles. Color change in iridescence has been controlled by applying electrical potential [32].

1.7.2 Conductive polymer coated latex particle

Conductive polymer of polypyrrole [75, 76], polyaniline [77] and poly(3,4-ethylenedioxythiophene) [78] coated latex particles has been synthesized and applied to the research of electrochemical mechanism. The suspension of PANi coated core-shell PS showed voltammetric curves controlled by diffusion of the particles. [79,80,81]. The current –voltage curves of particle suspensions are different from those of conventional PANi films in that no wave was found for the electrochemical transformation between the electric conducting and the insulating state [35].

1.7.3 Ferrocene immobilized latex particles

Various ferrocene dendrimers have been synthesized [82,83,84]. However, because of the limit of the synthetic methods and complicated synthetic processes, it is difficult to accommodate a large number of redox sites in one dendrimer molecule. Hence, constructing ferrocene immobilized latex is booming filed of physical chemistry .

The first latex containing ferrocene unit was reported by Ahamad and coworkers [85]. They synthesized a series of ferrocenyl latex by the copolymerization of styrene and vinylferrocene(VFc). They predicted the stability of the particle suspension with the *DLVO* theory. In his work, was used to determine whether particle aggregation had been caused by oxidation of the ferrocene moiety to ferrocinium. The peak splitting of Mössbauer spectroscopy was ascribed to the electron hoping between the ferrocene and ferrocinium sites in the polymer of latex.

The synthesis of core-shell vinylferrocene immobilized PS latex as well as electrochemistry was reported by Aoki group [86,87,42 ,]. VFc coated latex has a large numbers Fc unit on one particle. Since hydrophobic property of VFc and PS prohibit the ion transfer in aqueous suspension, the voltammogram had no redox waves. When using a nitrobenzene modified PG electrode as working electrode, the electrochemical activity was realized, and the whole processes consisted of diffusion of latex in aqueous phase, dissolution of particles in the nitrobenzene film and the electrode reaction of dissolved PVFv. In order to reduce the hydrophobicity of VFv-PS particle, sulfonate group was introduced in to the shell during the synthesis. The sulfonated VFc-PS particles adsorb on PG electrode showed a good adsorbed CV activity of Fc units in $NaBF_4$ aqueous solution. From the Faradic charge of Fc unit, the electroactive sites per particle were estimated to be 8% of the whole immobilized Fc units. A partial charge transfer electrode reaction model was proposed, in which the particles were adsorbed in hollows of the rough surface of the PG electrode.

The work on the dependence of electroactivity on the VFc-PS particle size was carried out by Aoki group. VFc molecule was adsorbed on various sized PS latex by the hydrophobic interaction between PS and the VFc. In the CV of latex aqueous suspension, the anodic peak current was controlled by diffusion of particle, and voltammetric peak current increased with an increasing of particle size for a given analytical concentration. The increase was explained in terms of combination of the uniform distribution of VFc in

the particle, the partial charge transfer and the small diffusion coefficient. Interesting result was that oxidation of VFc occurred in the restricted domain from a contacted point of particle with electrode. The whole mechanism of the reaction is diffusion of the particle to the electrode, the partial oxidation to VFc+, release of VFc+from the particle to the solution, and the reduction of released VFc+.

In order to obtain ideal core-shell ferrocene-containing latex particle, Chen and co-workers synthesized a kind of polyallylamine-ferrocene coated PS latex (PSPAA) with three steps of forming PS core, the polyallylamine-shell, and the ferrocenyl-shell [88]. The shell contains the amide group, providing a hydrophilic circumstance for the transfer of counter-ions. 2-propanol suspension of PSPAA showed diffusion controlled voltammetric current, which was smaller than the values calculated from the conventional multielectron-transfer equation with the known bulk concentration and the diffusion-coefficient of the latex [89] .

1.8 The aim of thesis

Ferrocene and ferrocene derivatives not only are stable organometallic compound [90] but also have reversible electrochemical responses, solvent-independent redox behavior and high ultraviolet absorption [91,92 93]. Based on these advantages of ferrocene molecule, various ferrocene-containing polymer had been synthesized with regard to application as diverse as electrocatalysis [94,95], reference electrode[96], electrochemical diodes [97] and secondary batteries [98]. In these extensive application, the synthesis of FcMA polymer and using it as modified materials of electrode were an indispensable exemplification [99,100].

In recent years, the research of constructing ferrocene immobilized latex particle has become attractive. Representational synthesis and electrochemical research was focus on vinylferrocene-immobilized polystyrene latex [42,43,44] and polyallylamine-ferrocene coated PS core-shell latex [45]. All of these manifest redox activities under a given experimental conditions. However, the high hydrophobic properties of polyvinylferrocene and high hydrophilic properties of polyallyamine-ferreocene limited the electrochemical research of two kinds of polymer coated latex in aqueous solution. So constructing an amphiphilic ferrocene immobilized latex become a subject of present thesis.

FcMA not only has a vinyl group which makes FcMA easy to be polymerized with other vinyl monomer, but also has a ester group which make FcMA hydrophilibility. If FcMA is immobilized on PS latex by polymerization it can avoid the high hydrophobic and hydrophilic properties of polyvinylferrocene and polyallyamine-ferreocene coated particles. However, no work has been reported on the immobilization of amphiphilic FcMA on latex particles.

In this dissertation, FcMA was immobilized on PS latex with the expectation that FcMA-PS latex exhibits ideal redox properties at an electrode in aqueous suspension. We synthesized FcMA immobilized PS latex particles with various size, characterized them by FT-IR, UV and cyclic voltammetric methods and investigated the size-effect of latex on the electrochemical activities of redox particles for obtaining the partial charge transfer model.

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Chapter 2

Preparation and electrochemical characterization of ferrocenyl-coated polystyrene monodispersed latex particle

2.1. Introduction

The electrochemistry of polymer colloids and macrobiomolecule with redox properties have received increasing attention [1, 2, 3], but the large particles such as enzymes, proteins [4], fullerene [5], metal nanoparticles [6], complex clusters [7] and colloids [8] often show dull electrochemical responses, such as broad voltammetric waves, large overpotentials, large irreversibility, and slowly responding current. Possible reasons for dull responses are chemical complications via a mediator, geometrical blocking of redox sites, sluggish charge propagation within particles, complicate transport of a particle by aggregation or adsorption. It is not easy to specify a definite reason, because there are no data describe relation of electrode behavior with size and geometry of large particles, to our knowledge. In order to obtain a relation between charge transfer and particle size, colloidal particles with simple mass transport have been synthesized, such as polyaniline-coated latex, aiming at immobilizing redox sites on latex particles. Unfortunately, the polyaniline coated latex exhibited voltammetric irreversibity because of slow propagation of conducting zone

Ferrocene and ferrocenyl derivatives are famous and important organometallic compound due to its stability, excellent electrochemical responds, solvent independent redox behaveior and high absorption of ultraviolet [9]. Numerous polymers, dendrimers with ferrocene moieties and some latex particles containing ferrocene unit have been prepared [10, 11], and these polymers and latex have been applied extensively to electrochemical research field. For example, the studies of the electrochemical behavior of Langmuir-blodgett (LB) ferrocene-containg polymer monolayer film modified electrode [12,13,14]; and the electrochemical behavior and the electrode reaction model of vinyl ferrocene immobilized polystyrene latex in suspension [15] . But we found the cyclic voltammogram of vinyl ferrocene polymer film modified electrode shows a broadened electrochemical feature [16]; and in order to obtain a favorable electrode reaction of vinyl ferrocene immobilized PS latex, some external assistance is needed,

such as modifying working electrode with nitrobenzene film and appending sulfonate unit in latex [14]. All these phenomena can be attributed to the hydrophobic property of vinylferrocene [15]. Chidsey et al have reported that ferrocene moieties with a polar ester group can show thermodynamically ideal surface electrochemistry whereas the non-polar ferrocene give a broadened electrochemical feature [17]. Finklea et al have also point out that the effect of polarity of the molecule on the cyclic voltammogram [18]. These concepts were validated via comparing the voltammetric behavior of LB film of ferrocenylmethanol acrylate (FcMA) copolymer with that of vinyl ferrocene copolymer [15]. But there are no reports about the distinction of voltammetric behavior of vinylferrocene coated latex and FcMA coated latex.

The aim of this chapter is to present a synthesis method of FcMA immobilized polystyrene latex (FcMA-PS), and discuss the voltammetric behavior of FcMA-PS in aqueous suspension.

2.2. Experimental

2.2.1. Materials

Styrene was purified with 5% aqueous NaOH and ion-exchanged water, dried with anhydrous Na_2SO_4 for 24 hours, distilled under vacuum at 35°C and stored in a refrigerator before it is used. Ferrocenylmethanol (TCI, Tokyo) and acrylyl chloride (Wako) were commercial available. Poly (N-vinylpyrrolidoin) (PVP) with a molar mass of ca 360 kg mol $^{-1}$ and α-azoisobytyronitrile (AIBN) were used as received. All the solvents were analytical grade and were distilled before used. Aqueous solutions were prepared by using ion-exchanged water.

2.2.2 Synthesis of monomer FcMA

With the document methods [19], to a anhydrous dichloromethane (20ml) solution of ferrocenylmethanol (1.08 g, 5 mmol), pyridine (1.4 ml) and acrylyl chloride (0.48 ml, 6 mmol) were add at 0°C. after stirring for 2h at 0°C, then, saturated NaHCO3 aqueous solution was added. The mixture was extracted with ethyl acetate, and dried with anhydrous $MgSO_4$. The product was purified by column chromatography of silica gel (200 – 400 mesh) with a mixture of hexane and dichloromethane (4:1, by volume) as eluent. The eluent was removed at reduced pressure to give an orange solid of FcMA (580 mg, 43% Yield).

2.2.3. Synthesis of ferrocenylmethanol acrylate coated PS latex

Firstly, we synthesized PS latex seed. The 100 ml ion-exchanged water containg PVP (1.5 g) was added to a 300ml three necked flask immersed in a thermostat bath at 70 ^{0}C, stirred vigorously and keeping N_2 flush throughout the reaction processes to ensure the oxygen was removed. 12 g cold styrene containing 0.15 g AIBN was added dropwise into reaction system for about 40 min. Polymerization proceeded at 70℃ for 24 h. After cooling the solution to room temperature, the milky polystyrene latex was obtained in suspension.

70 ml PS latex suspension was diluted with 50 ml water in 300 ml bottom flask. It was stirred overnight under N_2 , 2 ml benzene solution containing180 mg (0.44 mmol) FcMA and 0.25 ml styrene (2.3 mmol) was added drop by drop , reaction mixture was stirred vigorously at room temperature under the N_2 atmosphere for 24 h in order to facilitate FcMA and styrene anchor on the PS latex surface. Then AIBN (0.05 g) in 5ml 2-propanol was dropped into the mixture. The reaction system was maintained at 70°C for 24h. The color of mixture changed from white to yellow. The resulted suspension was rinsed with water 5 times by centrifugation and re-dispersion at room temperature, until we could not find the trace of FcMA unit in supernatant by cyclic voltammetry.

2.2.4. Electrochemical measurements and instrumentations

Cyclic voltammetry was carried out with a computer-controlled Potentio / Galvanostat (Model 1112, HUSO, Kawasaki). The electrode system consisted of a platinum working electrode 0.8mm in radius, an Ag / AgCl / 3.0 M NaCl reference electrode and a platinum coil counter electrode. The surface of the working electrode was polished with 0.5 μm alumina paste on wet cotton and rinsed with distilled water in an ultrasonic bath before each experiment.

2.2.5. Aanalysis of size, size-distribution and particle-dispersion

The size of FcMA-PS latex particle were determined by scan electron microscope (SEM,Hitachi S-2600H), sample were dried and Pt-Pd alloy sputter coated in order to become electron conductive. The size distribution and particle-dispersion were determined by a light scattering instrument (Malvern Zetasizer Nano-ZS).

2.2.6. Analysis of chemical composition

FT-IR spectra of FcMA, PS and FcMA-PS latex particles dispersed in KBr disk were recorded by Protege 360 (Nicolet). UV spectra were recorded with UV-570 spectrometer (Jasco, ToKyo).

2.3 Result and discussion

2.3.1 Determination of particle size, uniformity and stability

A SEM micrograph of particle is shown in Fig.2.1. it shows that the reaction produced particle have spherical morphology with a mean diameter of approximately 0.9 ± 0.05 μm. particle size by distribution of volume, number and intensity was1.054μm which were measured by light scattering method (Fig.2.2). Latex particle is uniform but we found size of latex was different between the above two methods, it can be attributed to the slightly shrinking of particle during the drying processes for preparing the sample or the errors of measurement of SEM; another reason maybe that latex can be swelled partially in liquid circumstance during storage. With 0.9 μm diameter, 1g particle have surface area of 6.35m^2, this large surface area is available site for the absorption of FcMA and styrene to proceed to copolymerize. The latex aqueous suspension can keep monodispersed states for several months, but if the concentration of electrolyte $(CH_3)_4NCl$ is lager than 1M, it can not maintain the stability for one day. So the electrochemical experiments must be finished at a shorter time, and the concentration of the supporting electrolyte should be as lower as possible.

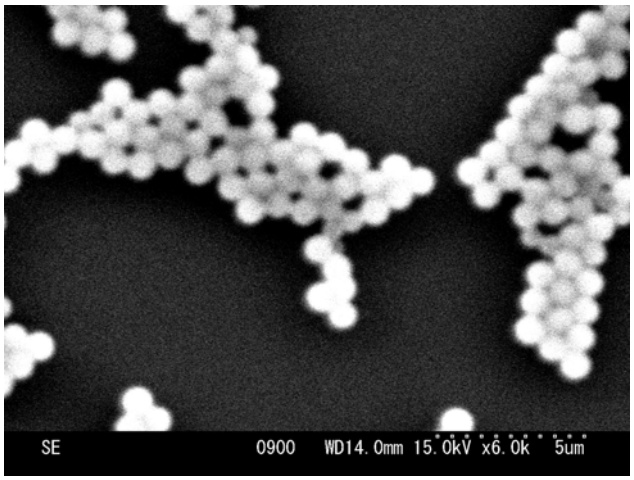

Fig.2.1. SEM micrograph of FcMA immobileized latex with diameter of 0.9±0.05 μm

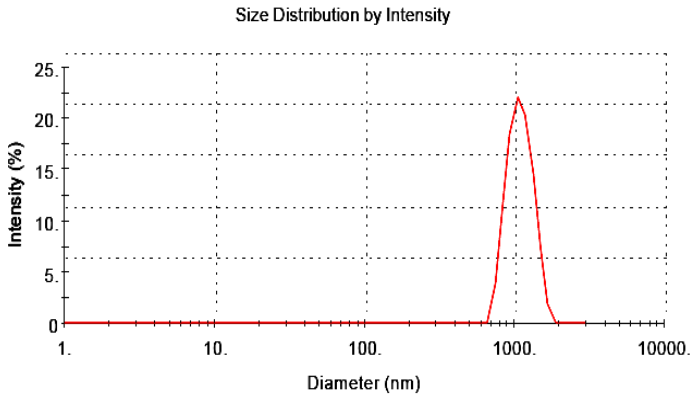

Fig.2.2. Size distribution of the FcMA-PS latex particle by intensity

2.3.2 Copolymerization

The PS latex is stabilized by the steric reagent PVP, this stabilized PVP layer and absorbed benzene provided a polymerization location where was similar to an organic circumstance or surface emulsion. The aim of long-time reaction is to ensure reaction yield of copolymerization, because when reactant ratio of FcMA to styrene is 1:5, the polymerization yield only 1.1% per hour [20].

2.3.3 Characterization of chemical composition

The latex suspension was rinsed with water by centrifugation and redispersion repeatedly, until there is no any CV signal of FcMA in centrifugated supernatant, then was redispersed in 60ml water. The yellow characteristics of FcMA-PS latex was assumed to the color of FcMA on PS latex. To identify the possibility, 1ml latex suspension was dried and weighed (0.0283g), dried latex particles were dissolved in 5ml dichloromethane, the UV spectrum of latex solution is shown in Fig.2.3. There are two main absorption bands, λ_{max} at 325nm and 435nm, they are accorded with the specific absorption of ferrocene unit [21]. Comparing the curve of absorption of FcMA and FcMA-PS latex particle, we can find no shift occurred at the position, λ_{max} =435nm, it identified that the electron structure of FcMA on latex did not change clearly and was similar to the monomer FcMA. From the UV spectrum we can also find FcMA unit is still at reduced state, if the ferrocene units were oxidized, there should appear a ferrocinium absorption at 610-630nm. So we use λ_{max} 435nm as reference position and FcMA monomer as standard compound to determine the amount of FcMA moieties per particle.

At the assumption of the density of FcMA-PS latex is equal to that of PS latex (1.05 g cm^{-3}), the calculated weigh of one of dried latex particle is 4.01×10^{-13}g, particle numbers of 1ml latex suspension is 7.06×10^{10} in present work. Referring the absorption

of dichloromethane solution of FcMA-PS latex, the concentration of FcMA moieties is 0.9mM, so the concentration of ferrocene moieties in aqueous suspension is 4.5mM, and the numbers of ferrocene unit per latex particle is 3.8×10^{7}.One particle have surface area 2.54μm^2, so one ferrocene unit takes an average area of 6.7×10^{-8}μm^2, if we think this area as a disc, and ferrocene unit at the centre of a circle, then average distance of ferrocene unit on latex surface is two times of radius of the disk, 2r = 0.29nm, near to 2 times of length of covalence(0.154nm)), but for the copolymerization of the styrene and FcMA, the several possible position of ferrocene unit was shown in Fig2.4, the average distance of ferrocene unit should be larger than the 2r, so on latex surface we did not constructed a monolayer, maybe a multilayer structure or some ferrocene unit distributed into latex. But it still mirrored FcMA was immobileized on PS seed successfully.

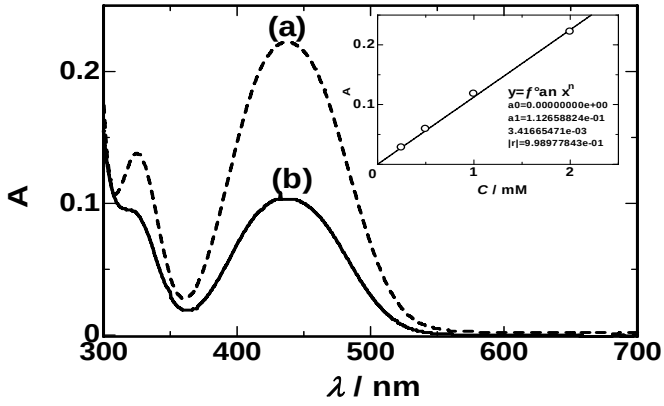

Fig.2.3. (a) UV of 0.2mM FcMA (dotted line); (b) UV of 1ml FcMA-PS latex suspension was dried and dissolved in 5ml dichloromethane(solid line) . And calibrated curve of FcMA (Inner figure)

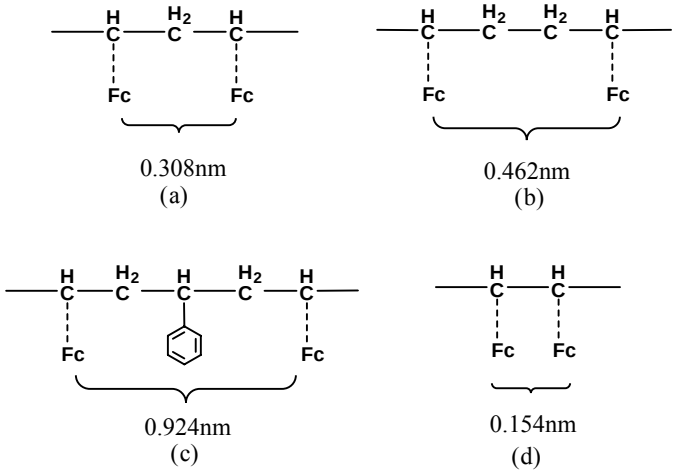

Fig.2.4. the image of distributive possibility of ferrocene unit in copolymer of FCMA and styrene on latex surface

The FT-IR of the FcMA and FcMA-PS latex is shown in Fig.2.5. The band combination of FcMA-PS latex and FcMA monomer at 1000-1100 cm^{-1} are attributed to the monosubstituted ferrocene. the cyclopeantadienyl rings' CH out-of-plane deformation of latex particle at 810cm^{-1} is reduced through comparing it with monomer FcMA, the reason maybe come from the bondage of the copolymer chain [20]. The carbonyl stretching band of FcMA-PS latex at 1734cm^{-1} is close to that of monomers', but it was widened, maybe resulted from the cooperation of carbonyl group in FCMA-PS latex and in resident PVP on the latex surface. 1625-1635 cm^{-1} bands are complicated double band stretching, 2990-3000 cm^{-1} are cyclopeantadienyl rings' CH stretching. For FcMA-PS latex, it maybe bundled some dispersion medium or carbonyl connected with water by hydrogen bond, so at the region of 3400 cm^{-1}, the transmittance of FcMA-PS latex become stronger. Herein, the immobilization of FcMA is identified by FT-IR spectrum too.

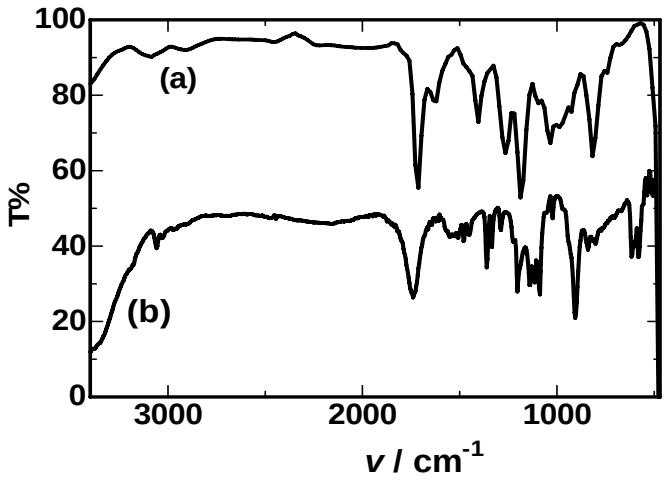

Fig.2.5. FT-IR spectrum of (a) FcMA monomer; (b) FcMA-PS latex

2.3.4 Electrochemical behavior of FCMA-PS particle

Another evidence of FcMA had been immobilized on latex particle is the electrochemical behavior of FcMA-PS particle in aqueous suspension (shown in Fig.2.6.). Firstly, the CV of surfactant obtained by centrifugation did not showed any redox peaks (Fig.2.6c.); Secondly, comparing Fig.2.6.a and 2.6.b, we can find a pair of simple redox waves at 0.271 / 0.207V in the CV of FcMA-PS suspension, and redox pairs of FcMA monomer in PVP aqueous solution (1.5gdm^{-3}) appeared at more negative potential. Therefore, the redox waves of FcMA-PS latex suspension come from ferrocene moieties

on FCMA-PS and not from the dissociated FcMA monomer or released FcMA moieties from FCMA-PS latex.

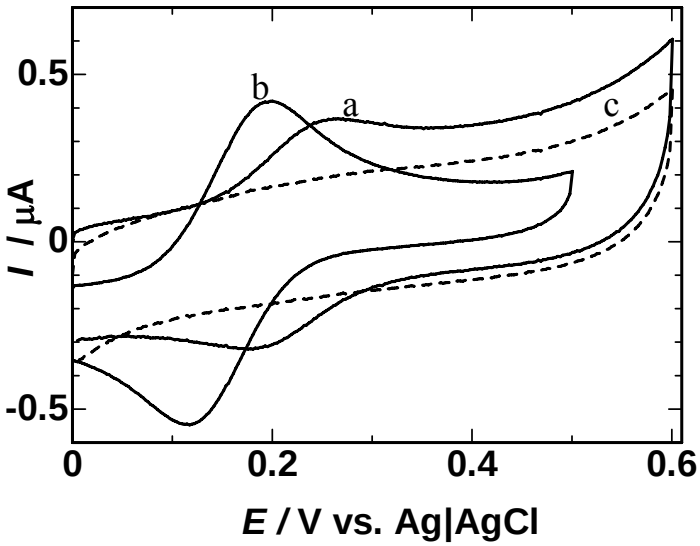

Fig.2.6. Cyclic voltammograms of (a) FcMA-PS suspension including 28mg/cm^3 dried latex, (b) FcMA in the surfactant (1.5 g/dm^3 PVP) contained aqueous solution, and (c) the supernatant of the suspension by the centrifugation. They were obtained in the 0.05 M $(CH_3)_4NCl$ aqueous solution on Pt disk electrode 1.6 mm in diameterat scan rate of 0.1 V s^{-1}.

The kinetics of the voltammetric behavior of latex suspension was investigated by varying the scan rate in 0.05M $(CH_3)_4NCl$ aqueous suspension. The peak current increased with the increasing of the scan rate and without potential shift (Fig2.7). Fig.2.8 show the dependence of anodic, I_{pa} , and cathodic, I_{pc}, peak currents on the potential scan rate, v, anodic and cathodic is proportional to the square root of scan rate. This suggested electrode reaction process of FcMA-PS latex in suspension is diffusion-controlled. Peak current ratio I_{pc} / I_{pa} is about 1, which means the oxidation and reduction reaction both are carried out on latex surface, oxidized FcMA moieties did not broke away from bulk latex particles.

Peak current of the succeeding n-electron reaction can be expressed by [22]

$$I_p = 0.446nF^{3/2}c^*A(Dv/RT)^{1/2} \quad (1)$$

Where c* is the bulk concentration of particle suspension, A is the electrode surface area, D is the diffusion coefficient of particle, on the assumption of hard sphere model, D can be estimated by Stokes-Einstein relation [23] , $D = K_BT/6\pi\eta a$, where η is the viscosity, was taken to be 0.891×10^{-3} Kg m^{-1} s^{-1} , and K_B is Boltzmann's constant. In equation (1),

the I_{pa} / $v^{1/2}$ can be obtained from Fig.2.8, bulk concentration, c*, is known, so we can calculated the numbers of succeeding n-electron. The resulted numbers is not equal to the numbers obtained by UV, means only 30% take part in electrode reaction, it is partial charge transfer electrode reaction.

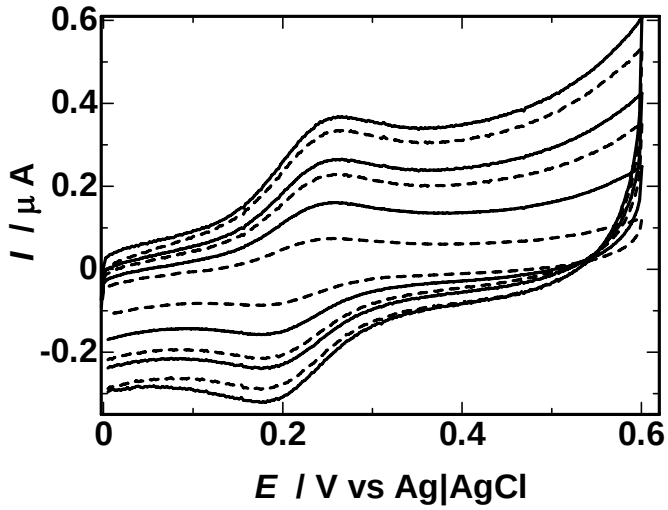

Fig.2.7 Cyclic voltammograms of FcMA-PS suspension including 28mg/cm^3 dried latex with scan rate of 100,80,60,50,40,30,10mVs^{-1}

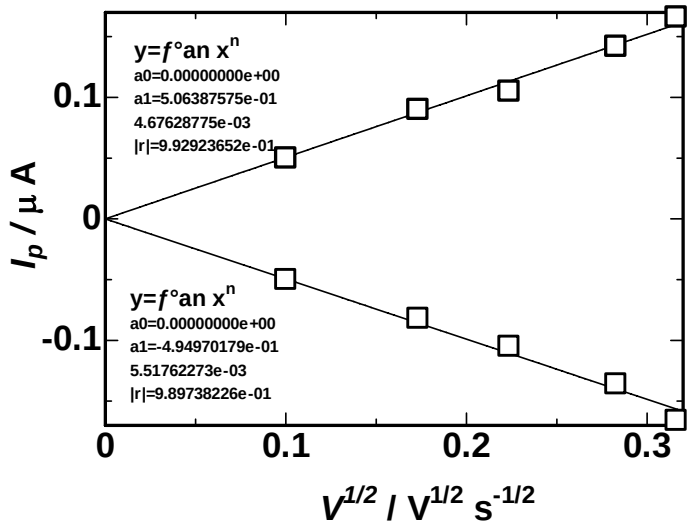

Fig.2.8. Variation of the peak currents of the Fig.2.7 with the square-root of the potential scan rate.

2.4 Summary

In summary, a type of uniform and monodiespered FcMA-PS latex has been fabricated successfully through the copolymerization of FcMA and styrene on PS latex seed. The morphology, chemical composition and electrochemical properties have been characterized by SEM, light scattering method, FT-IR, UV and cyclic voltammetry. Due to ferrocene moiety connected a polar ester group, FcMA-PS particle is electroactived in

aqueous media, anodic and cathodic peak current are proportional to the square root of scan rate, electrode reaction processes is diffusion-controlled and partial charge tranfered. The partial charge transfer might be ascribed to the thickness of double layer less than particle diameter. More reasonable interpretation of partial charge transfer and structure of FcMA-PS latex should be investigated in terms of the various sized particles.

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Chapter 3

Size-dependent efficiency of electron transfer at suspended ferrocenyl jumbo particles

3.1. Introduction

Voltammetric work on large redox particles such as metal nanoparticles [1- 5] and redox latexes [6- 10] is interesting in that they may exhibit unusual properties owing to molecular interaction or assemblies. For example, thiolate ligand-stabilized clusters with Au cores have showed the quantum dot properties of monolayer-protected clusters [1], quantized double layer charging [2] and the appearance of a molecule-like bandgap [3]. The stabilities of silver alkylcarboxylate composing of the nanoparticles have decreased with an increase in the length of alkylchains owing to the interaction with the core silver metal [5]. Dispersed polyaniline latex at the microelectrode with similar size to the latex diameter has showed discretized currents [6]. Hemin-immobilized polyallylamine-polystyrene latex suspensions have shown higher catalytic activity for dioxygen [7] and carbon dioxide [8] than molecular hemin has. Polyaniline latex has protected strongly against corrosion [11,12]. Potential cycling of polypyrrole latex has varied a degree of adsorption of imidazole [13]. Advantages of voltammetry for jumbo particles have been demonstrated to be not only easy identification of redox sites by peak potentials [14] but also evaluation of transferring charge per particles [9,10,14].

Voltammetric measurements, however, have some technical difficulties in poor dispersion of particles in electrolyte solution [15], in less reactivity of owing to surfactants or hydrophobic surface of particles [16], and in purification of suspensions. Furthermore, an essential problem lies in the concept of which reaction actually occurs [17], $R_n \leftrightarrow O_n + ne^-$ or $n(R \leftrightarrow O + e^-)$ even in equilibrium. More complications can be included in currents owing to not only translational diffusion of particles but also rotational diffusion [18], partial electron transfer of the redox sites on the particle surface in contact with an electrode [9,10], detachment of redox sites from particles [9], and charge transport within particles. They ought to depend not

only on size of particles but also distribution of redox sites within one particle. Consequently, it is necessary to control the distribution.

There are basically two types of distribution: one being the core-shell structure at which redox sites are included only in the shell, the other being uniform distribution of redox sites over the particle. The former has been realized in metal nanoparticles by coating metal core with surfactants [1,4]. The core-shell structure of redox latex particles has been formed by coating hydrophobic cores with hydrophilic shells [7,10,19]. In contrast, latexes with uniform distribution has been constructed by adsorbing redox sites into particles [9,16]. Unfortunately, the adsorbed redox sites were readily desorbed by redox reactions, like corruption of redox micelles after redox reactions [20,21]. It is necessary to immobilize the redox moiety with a sigma bond on polymers of the core in order to stabilize the redox sites against desorption. Although very hydrophobic redox moiety may make the redox distribution uniform in a polystyrene core, no redox reaction occurred in the strongly hydrophobic environment [16]. Moderate hydrophobicity may be required both to make the distribution uniform and to facilitate redox reaction. We select ferrocynylmethanol acrylate for a candidate of satisfying both conditions in the present work, and attempt to synthesize uniformly distributed latexes with various diameters. The voltammetric responses of the particles in aqueous suspensions are examined in the context of partial electron reactions [9,10].

3.2. Experimental

3.2.1 Chemicals

Styrene was purified with 5 % aqueous NaOH solution and distilled water, dried with anhydrous $MgSO_4$ for one day, distilled under vacuum at 35 ^oC, and then stored in a refrigerator before use. Ferrocenylmethanol (TCI, Tokyo), acrylyl chloride (Wako), poly(n-vinylpyrrolidone) (PVP) with 360 kg mol^{-1} and α,α'-azoisobutyronitrile (AIBN) were used as received. All solvents were analytical grade and distilled before use. Aqueous solutions were prepared with ion-exchanged and twice-distilled water.

3.2.2 Synthesis of ferrocenylmethanol acrylate (FcMA)

The FcMA was synthesized through the Schotten-Baumann reaction [22], as is shown in Fig. 1. Ferrocenylmethanol (1.08 g, 5 mmol) and pyridine (1.4 cm^3) were added to anhydrous dichloromethane (50 cm^3) at 0 ^oC. Acrylyl chloride (0.48 cm^3, 6 mmol) dichloromethane solution (10 cm^3) was added drop-wise into the mixture. The mixture was stirred at 0 ^oC for 2 h to obtain pyridine chloride as white deposition of pyridine chloride. The deposition was filtered out and the filtrate was rinsed with saturated $NaHCO_3$, NaCl solution and water in turn, extracted by ethylacetate, and dried with $MgSO_4$. The product was purified by column chromatography of silica gel (200-400 mesh) with a mixture of hexane and dichloroethane (4:1 volume). The eluent was evaporated to produce an orange solid of ferrocenylmethanol acrylate (581 mg, 43 % yield). The bands of FTIR on a KBr plate were 3110, 2980-2860, 1724, 1625, 1635, 1460, 1400, 1385, 1280, 1190, 1115, 1050, 994, 820 and 740 cm^{-1}. ^1H NMR chemical shifts at 300 MHz referenced with $CDCl_3$ were in accord with the literature [23]: δ6.41-6.11 (2H, $C=CH_2$), δ5.71 (1H, CH=C), δ4.90 (2H, $-CH_2-$), δ4.10-4.75 (9H, Cp-H).

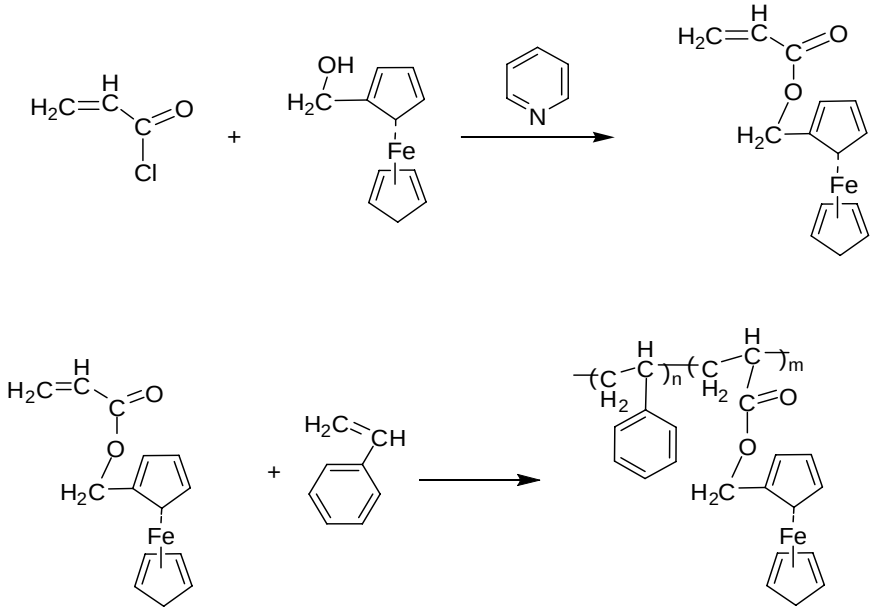

Fig.1 Reaction scheme of synthesis of (upper) FcMA and (lower) ferrocenyl moiety-immobilized latex particles.

3.2.3 Synthesis of FcMA/styrene copolymer

FcMA (540 mg, 2 mmol), AIBN (8 mg, 0.05 mmol) and styrene (250 mg, 2.4 mmol) were added to dearated benzene (25 cm^3) under nitrogen environment. The mixture was stirred for 24 h at 70^oC to polymerize the monomer completely and cooled to room temperature. Petroleum ether (50 cm^3) was added drop-wise to the cooled mixture to precipitate the yellow copolymer, which was filtered, rinsed with a mixture of petroleum ether and benzene (2:1 volume) repeatedly and vacuumed to be dried. The ferrocenyl group was identified by UV-vis spectra of which specific band was at 435 nm [24].

Table 1. Amounts of the reactants, surfactants and solvent for the polymerized PS latex

2*a* μm	2-propanol cm^3	Styrene cm^3	SDS G	$NaHCO_3$ g	H_2O cm^3	KPS g	PVP g	AIBN g
0.084	0	2.5	0.8	0.084	100	0.005	0	0
0.200	0	6.0	0	0.084	100	0.005	1.5	0
0.520	0	6.0	0	0	100	0.005	1.5	0
0.720	0	10.0	0	0	100	0	1.5	0.15
0.770	15.0	10.0	0	0	100	0	1.5	0.15
1.13	15.0	12.0	0	0	100	0	1.5	0.15
1.54	15.0	15.0	0	0	100	0	1.5	0.15
1.67	15.0	15.0	0	0	100	0	1.5	0.15

3.2.4 Synthesis of ferrocenylmethanol acryate-coated PS latex

Polystyrene (PS) latex was prepared by the previous method [16]. The size of PS particles was controlled with concentrations of styrene, of AIBN (a radical initiator), and of SDS or PVP (steric stabilizer). The conditions were summarized in Table 1. The particle became larger with an increase in the ratio of 2-propanol to water, because high amount of 2-propanol promotes growth of the seed latex [25].

The milky white PS suspensions (70 cm^3) including the dried PS (1.6 g), was diluted with 50 cm^3 water in a 300 cm^3 round bottom flask. A 2 cm^3 mixture of benzene solution containing 180 mg (0.44 mmol) FcMA and 0.25 cm^3 styrene (2.3 mmol) was added drop-wise into the suspension. The mixture was stirred vigorously

at room temperature under N_2 for 24 h (Fig. 1). Then 5 cm^3 AIBN (0.05 g, 0.9 mmol) and PVP (0.3 g dm^{-3}) aqueous solution was added to the suspension drop-wise. The mixture was maintained at 70 °C for 24 h. The color of the suspension changed from white to yellow. The yellow suspension was centrifuged and re-dispersed with water until no trace of FcMA in the supernatant was detected by cyclic voltammetry. The purification was repeated usually five times. The latex suspension in distilled water was stored in a refrigerator before use. The size distribution of the PS particles was determined by the light scattering (in Fig. 2A) and microscopy (Fig. 2B) in water.

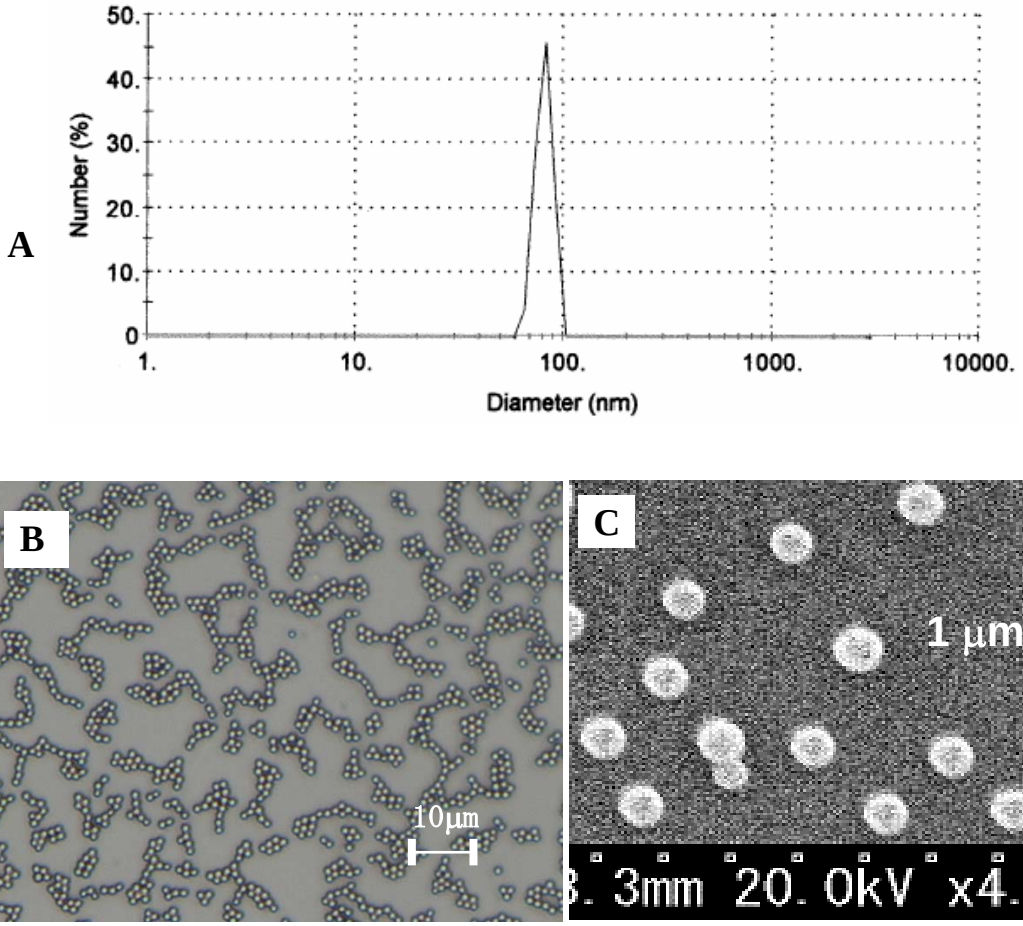

Fig.2. (A) Size distribution of the FcMA-PS aqueous suspension of particles with 0.84 μm in diameter, measured with the light scattering instrument, (B) photograph of the dried sample of the aqueous suspension 0.72 μm in diameter by the optical microscope and (C) SEM photograph of the dried particles after dispersed with an excess amount of PVP.

3.2.5. Measurements and instrumentation

Cyclic voltammetry was carried out with a computer-controlled Potentio/ Galvanostat (Model 1112, HUSO, Kawasaki). The working electrode was a platinum disk 0.8 mm in radius. The reference electrode was an Ag|AgCl(3.0 M NaCl), and the counter electrode was a platinum coil. The surface of the working electrode was polished with 0.5 μm alumina paste on a wet cotton and was rinsed with distilled water in an ultrasonic bath before each voltammetric run.

The size of the latex particles was determined by scanning electron microscopy (SEM, Hitachi, S-2600H). The size distribution and particle-dispersion were determined by a light scattering instrument (Malvern Zetasizer Nano-ZS) and a video microscope, VMS-1900 (Scalar).

FT-IR spectra were obtained from a Protege 360 (Nicolet). UV spectra were recorded with UV-570 spectrometer (Jasco, ToKyo). The ^{1}H NMR data were obtained with JNM-EX400 (Hitachi). The average molecular weight was determined by gel permeation chromatography (GPC).

3.3. Results and discussion

3.3.1 Properties of FcMA-PS latex

FcMA exhibited voltammetric peaks at 0.126 / 0.061 V, as is shown in Fig. 3. The potential difference between the anodic and cathodic peaks was 65 mV at the scan rate, v = 0.01 V s^{-1}, indicating the electrochemical reversibility. The reversibility is due to the ferrocene moiety in FcMA. The anodic and cathodic peaks current were proportional to the square root of the scan rate, v, (in the inset of Fig. 3) implying the diffusion-controlled process. The value of the diffusion coefficient was calculated from the slope [26] to be 5.51×10^{-6} cm^2 s^{-1}.

GPC of the FcMA/styrene copolymer in CH_2Cl_2 showed an average molecular weight of 230 000, with standard polystyrene used as the calibration. The mole ratio of the ferrocenyl group to the styrene group in the copolymer was determined [16] by UV spectroscopy to be 0.26. This value indicates that a unit is composed of one

ferrocenyl moiety and four styrene moieties (m/n = 4 in Fig. 1).

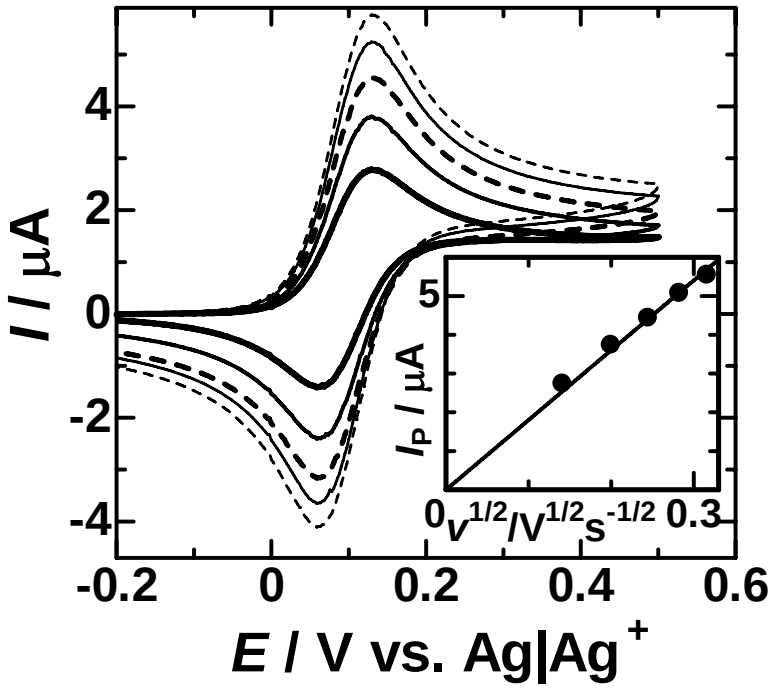

Fig.3. Voltammograms of 1.5 mM FcMA in 0.1 M $TBAPF_6$ of dicholomethane solution at the Pt (d=1.6mm) electrode at the scan rates of v = 100, 80, 60, 40 and 20 mV s^{-1}. The inset is the plot of the anodic peak current I_p against $v^{1/2}$.

The yellow color of the FcMA-PS latex is obviously ascribed to the ferrocenyl moiety. A tetrahydrofuran solution including a given amount of the dried latex was spread on the electrode and dried to form a film. The concentration of the ferrocenyl moiety in the film 0.75 μm thick was evaluated to be 21 mM. The voltammogram of the film-coated electrode in water, acetonitrile, or 2-propanol did not exhibit any redox wave in the potential domain from 0.0 to 1.0 V. When the film was immersed in acetonitrile including 0.1 M $TBAPF_6$ solution for more than 2 h, the voltammetric wave appeared at potentials close to those of the FcMA monomer and its current increased with the immersion time until 6 h. The peak currents were proportional to $v^{1/2}$ and hence were diffusion-controlled. The diffusion coefficient value or the apparent one of the ferrocenyl moiety in the copolymer was D_{cop}, = 3×10^{-9} cm^2 s^{-1} for the 6 hs' immersion.

The FcMA-PS latex was dispersed well in aqueous solution without adding any

surfactant deliberately. The aqueous suspension was stable for six months without appreciable sedimentation when it included no electrolyte under nitrogen atmosphere. The particles in the suspension were spherical with common diameter from the view by the optical microscope (Fig. 2B). Some tens particles were adhered each other to groups like spawn during the evaporation of water. The SEM photograph of the dried FcMA-PS latex particles on a glass plate is shown in Fig. 2C. The average diameters, $2a$, of the particles are listed in Table 2. The diameter was slightly larger than that from the optical microscope, probably because of the evaporation of solution from inside of the particles in the vacuum process.

Table 2. Parameters of the FcMA-PS particles

$2a$ / μm	n_{uv} $\times 10^{-6}$	$D\times 10^{9}$ / cm^2s^{-1}	$W_{particle}$ $\times 10^{15}$/ g	n_{cv} $\times 10^{-6}$	n_{cv}/n_{uv}
0.084±0.0	0.015	58	0.32	0.014	0.94
0.20±0.04	0.397	24	4.40	0.353	0.89
0.52±0.04	7.11	9.42	77.3	4.05	0.57
0.72±0.08	23.7	6.81	205	10.2	0.43
0.77±0.08	21.3	6.37	250	7.98	0.38
1.13±0.08	77.9	4.34	793	26.1	0.36
1.54±0.08	202	3.18	2010	55.3	0.27
1.67±0.012	262	2.93	2560	66.2	0.25

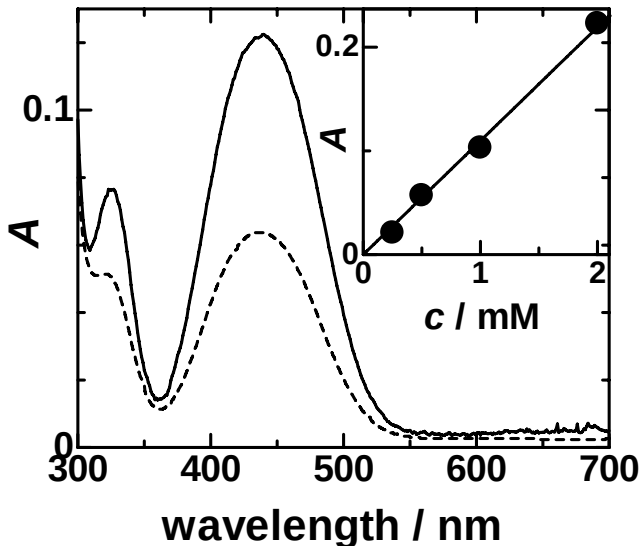

Fig.4. UV spectra of the FcMA-PS (solid curve) and FcMA (dotted curve) dissolved in CH_2Cl_2 solution. The inset is the plot of the concentration of FcMA against the absorbance at 435 nm

The dried FcMA-PS particles were dissolved in CH_2Cl_2 without any residue to get a transparent, yellow solution. Figure 4 shows the UV spectra of FcMA-PS particles and of FcMA dissolved in CH_2Cl_2. The spectral band for the solution of the FcMA-PS particles at 435 nm was identical with that of the FcMA. The absorbance was proportional to the concentration of the particles. Immobilized FcMA should be in the reduced state of ferrocenyl moiety because the UV spectra did not showed any absorption (at 628 μm [27]) specific to the ferricenium moiety. The supernatant of the FcMA-PS suspension showed no absorption band of FcMA, implying that there should be no free FcMA in the suspension. The amount of ferrocenyl units per particle was determined quantitatively with UV spectroscopy by comparing the absorbance of dichrolomethane solution of FcMA-PS latex with that of FcMA [28,29]. The weight per particle was calculated from the diameter and the density of PS (1.05 g cm^{-3}) on the assumption that the density was identical with the bulk polystyrene. A given volume of the suspension was dried and weighed. The number of FcMA moiety per particle, n_{uv} , was estimated from $(4\pi/3)a^3$ and the concentration of the particle in the suspension, and is listed in Table 2. The values of n_{uv}, increasing with an increase in the radii, are plotted against a on the logarithmic scale in Fig. 5. They are on a line with a slope of 3.05. Consequently we can express n_{uv} as

$$n_{uv} = 4.5 \times 10^8 (a / \mu m)^{3.05} \qquad (1)$$

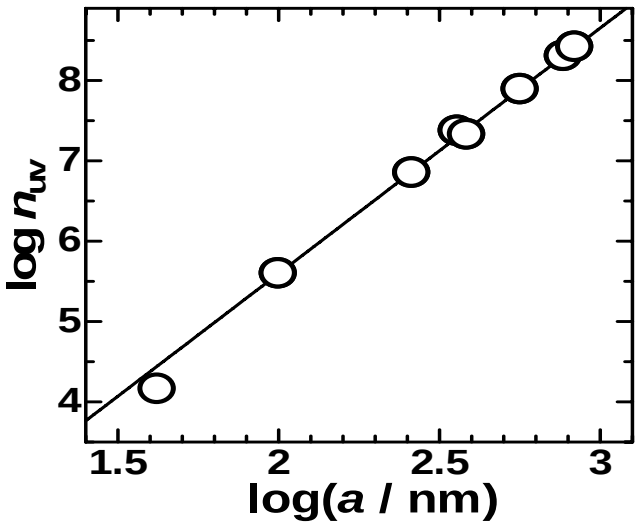

Fig.5. Logarithmic plot of n_{uv} against a.

The relation with the cubic radii indicates that the FcMA moiety should be distributed

uniformly even inside the particles. The value of the slope gives the concentration of FcMA moiety in the particles to be 0.18 M if the order of *a* is assumed to be 3. This value of the concentration corresponds to the volume 0.107 nm^3 occupied by one FcMA moiety or to the distance between closest neighboring FcMA moieties 0.48 nm within a particle.

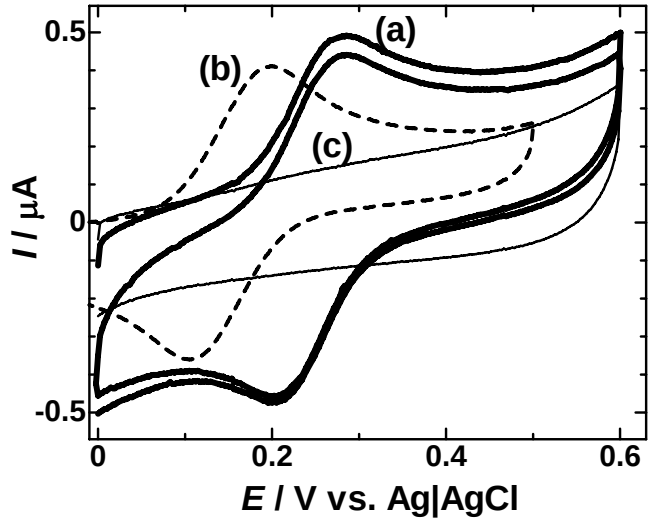

Fig.6. Cyclic voltammograms of (a) aqueous suspension including 0.028 g cm^{-3} dried FcMA-PS particle (2a = 0.77 μm), (b) FcMA monomer including 1 w% PVP aqueous solution, and (c) the supernatant of the suspension-(a) by the centrifugation under the conditions of supporting electrolyte of 0.1 M $(C_2H_5)_4NCl$ for v = 0.1 V s^{-1} at the Pt disk electrode.

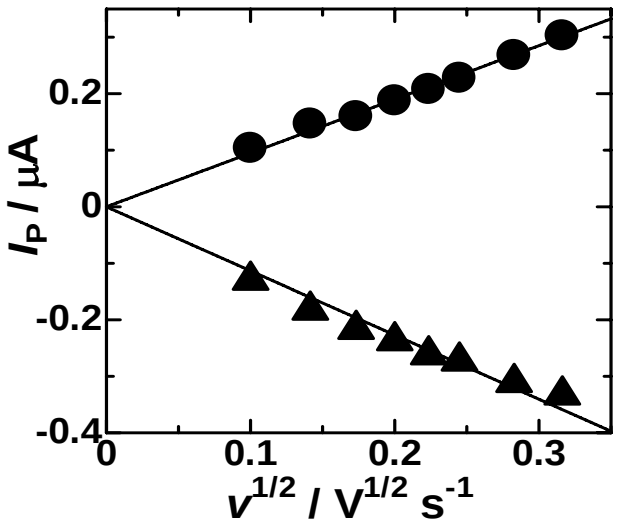

Fig.7. Scan rate-dependence of the peak currents, $I_{p,A,}$(circles) and $I_{p,C,}$(triangles), in 0.1 M $(C_2H_5)_4NCl$ aqueous suspension including 0.018 g cm^{-3} dried FcMA-PS 0.77 μm in diameter.

3.3.2 Voltammetry of FcMA-PS suspensions

The aqueous suspension of FcMA-PS including 0.1 M $(C_2H_5)_4NCl$ was electroactive at the platinum disk electrode in the potential domain from 0 to 0.6 V, as shown in Fig. 6(a). A pair of the redox waves at 0.27 / 0.20 V is ascribed to a couple of the ferrocenyl and the ferricenium moieties. The monomer FcMA in water including PVP showed the redox waves at 0.19 / 0.11 V (Fig. 6(b)). The negatively potential shift may be ascribed to redox interaction between neighboring ferricenium ions owing to the high concentration (0.18 M) within the particle. The voltammogram of the supernatant centrifuged at 20000 *g* for 30 min did not show any redox wave (Fig. 6(c)). Comparison with the three curves demonstrates that the redox wave (a) is not due to the free FcMA moiety or fragments of copolymer detached from the latex, but due to the immobilized ferrocenyl moiety. The difference between the anodic and the cathodic peak potentials (60 mV) is close to the diffusion-controlled reversible one (60 mV), as is in accord with the ferrocenyl moieties with a polar ester group [30-32]. The anodic and cathodic peak currents were proportional to the square-root of the scan rate, as is shown in Fig. 7, except for the anodic peak at the smallest two particles. Thus, the most of peak currents are controlled by diffusion of the particles rather than adsorbed particles or fragments. In deed, we did not view any adsorbed particle on the surface of the electrode both before and after applied potential by the optical microscope.

We estimate the dependence of the peak current on the radii through the expression for the diffusion-controlled current of multi-electron transfer [17]:

$$I_p = 0.446Fn_{uv}cA(DvF/RT)^{1/2} \qquad (2)$$

where D is the diffusion coefficient of the particle, c is the concentration of the particles in the suspension, and A is the electrode area. The variables depending on the radii of the particles are n_{uv} and D. The former has the dependence of $a^{3.05}$ through Eq. (1), whereas the latter varies with $a^{-1/2}$ through the Stokes-Einstein relation ($D = k_BT/6\pi\eta a$) [33], where η is the viscosity of the suspension. Consequently, the peak current ought to have the power of 2.55 in radii. We rewrite Eq.(2) as

$$\left(I_p v^{-1/2} c^{-1}\right)_{exp} = 0.446Fn_{uv}A(DF/RT)^{1/2} \qquad (3)$$

so that the term on the left hand side can be determined experimentally. In order to confirm the power, we plotted values of $I_p v^{-1/2} c^{-1}$ against a on the logarithmic scale in Fig. 8, where values of $I_p v^{-1/2} c^{-1}$ were obtained from the slopes of the plots of I_p vs. c

and vs. $v^{1/2}$ at a given value of a. All the points fell on a line, of which slope was 2.23. This is a size effect on the peak current. Although this value is close to 2.55, the variation (dashed line) of the right hand side of Eq.(3) evaluated from D (Stokes-Einstein relation) and n_{uv} (Fig. 5) is larger than the experimental one. The loss of the current value suggests the partial electron transfer of the latex [9,10], as below.

It is not easy to understand the size effect on the current, and hence we replace the current by the number of actually reacting charge per particle, n_{cv}, defined by

$$n_{cv} = I_p / 0.446FcA\left(DvF/RT\right)^{1/2} \qquad (4)$$

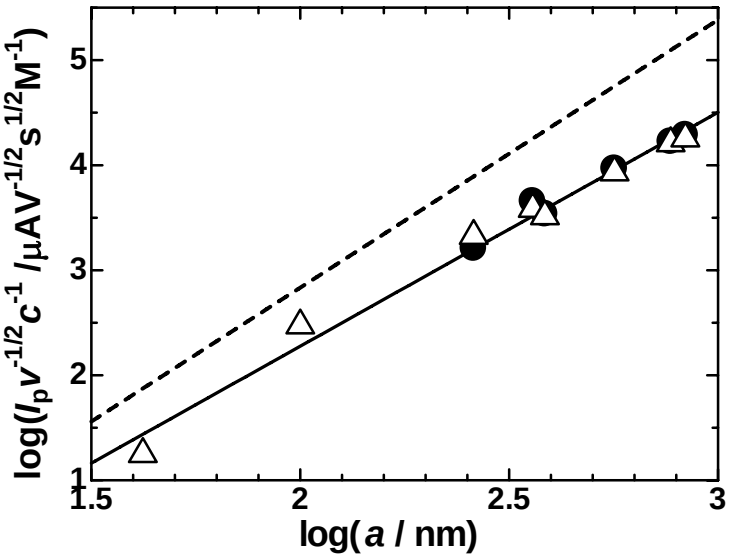

Fig.8. Logarithmic dependence of $I_p v^{1/2} c^{-1}$ on a for the anodic (circles) and cathodic (triangles) peak currents. The slope (regressed solid line) is 2.23. The dashed line was evaluated from Fig. 6 and the Stokes-Einstein relation by use of Eq.(3), of which slope is 2.55.

We evaluated n_{cv} from known values of D and $I_p v^{-1/2} c^{-1}$, and plotted the ratio n_{cv}/n_{uv} against a on the logarithmic scale in Fig. 9. The points fell on a line with a slope of -0.47. The ratio means the efficiency of the electrode reaction. The efficiency decreases with an increase in the radii. Since $n_{cv}/n_{uv} = 1$ at $a = 60$ nm (arrow in Fig. 9), all the redox electrons per particle for $a < 60$ nm can react without hindrance. The value -0.47 reminds us of the relation, $n_{cv}/n_{uv} = k_1 a^{-0.5} + k_2$ for the current controlled by rotational diffusion as well as translational diffusion of jumbo redox particles obtained by the Monte Carlo simulation [18]. Since the simulation has been based on the

assumption of surface-localized redox charge rather than the volumetric distribution, the application to the present latex is not reasonable. Nevertheless, if the ferrocenyl moieties in a given thickness from the surface are oxidized through electron exchange reactions within a particle, the rotational diffusion model may be rationalized, as is illustrated in Fig. 10. The high concentration (0.18 M) of the ferrocenyl moiety can facilitate electron exchange reactions in the particle to yield apparent diffusion of the ferrocenyl moiety. However, estimation of the diffusion thickness might need data of not only the apparent diffusion coefficient of the ferrocenyl moiety in the particle but also a retention period of the particle on the electrode for diffusion.

The other type of the n_{cv}/n_{uv} vs. a variation has been reported for the core-shell structured ferrocenyl latex [10], in which the shell was composed of hydrophilic polyallylamine and ferrocenylamide. Since the ferrocenyl moiety is localized only on the surface owing to the repulsion between hydrophobic PS in the core and hydrophilic polyallylamine in the shell, n_{cv} should be proportional to a^2. Consequently, the logarithmic plot in Fig. 9 (open circles) shows the power -1.47 which is close to the theoretical value -0.5-1= -1.5, consistently.

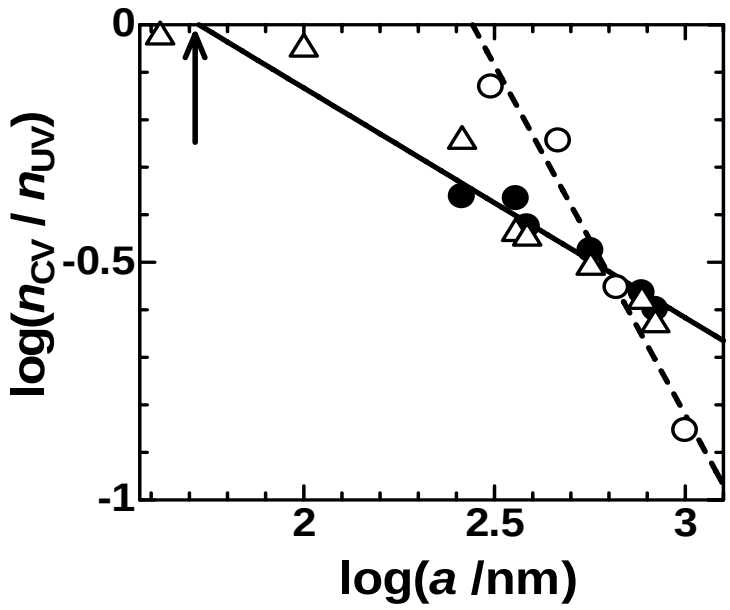

Fig.9. Logarithmic variation of n_{cv}/n_{uv} with a for the anodic (filled circles) and the cathodic (triangles) peak currents. The arrow points the intercept for $n_{cv}= n_{uv}$. The redox core-shell latex (open circles) showed the power -1.47 [10].

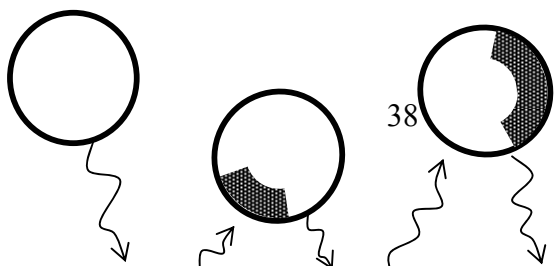

Fig. 10 Image of rotational and translational diffusion of a redox particle. The black shade in particles means the moiety oxidized at the electrode by collision with the electrode. Arrows represent directions of rotation and translation

3.4 Surmmary

The synthesized FcMA latex particles with diameter ranging from 0.084 to 1.7 μm had ferrocenyl moiety of which amount per particle was proportional to their radii. The proportionality suggests the uniform distribution of ferrocenyl moiety over the particle. The concentration of the moiety was 0.18 M, corresponding to the average distance, 0.48 nm, between the closest neighboring moieties. This distance may readily bring about redox interaction to induce the electron exchange reaction between neighboring ferrocenyl and the ferricenyl moiety. The high concentration is ascribed to high permeation and accumulation of the hydrophobic FcMA into the hydrophobic polystyrene particle.

The aqueous suspensions of the latex exhibited reversible voltammetric waves. The anodic and the cathodic peak currents were controlled by diffusion of the particles. Since D and n_{uv} are proportional to $a^{-1/2}$ and a^3, respectively, the diffusion-controlled current should be proportional to $a^{5/2}$. The observed power of a was 2.23 rather than 2.50. When the size effect is expressed as n_{cv}/n_{uv}, the proportionality of n_{cv}/n_{uv} to $a^{-0.47}$ suggests the larger contribution of rotational diffusion to the current for larger particles.

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Chapter 4

Conclusion

In order to investigate the electrode reaction of large particle, the FcMA (ferrocenylmethenol acrylate) immobilized PS (polystyrene) latex particles (FcMA-PS) with various diameters were synthesized by emulsion polymerization via PS as seed. The particles were almost spherical, monodispersed, and electrochemical active in aqueous suspension through characterization of SEM, light scattering methods, UV and cyclic voltammetric (CV) methods. The hydrophilic property of latex particle was increased partially by introducing of ester group on latex particles surface, therefore the FcMA immobilized latex aqueous suspension exhibited a better redox behavior at conventional Pt electrode. The peak current of large particle (2a = 0.9 μm) was proportional to the square root of scan rate, the electrode reaction was diffusion-controlled. Ferrocene units in one latex particle determined by CV were different from it determined by UV, that meant electrode reaction of FcMA-PS latex is partial charge transfered.

The synthesized FcMA-PS latex particles with diameter ranging from 0.084 to 1.7 μm had ferrocenyl moiety of which amount per particle was proportional to their radii. The proportionality suggests the uniform distribution of ferrocenyl moiety over the particle. The concentration of the moiety was 0.18 M, corresponding to the average distance, 0.48 nm, between the closest neighboring moieties. This distance may readily bring about redox interaction to induce the electron exchange reaction between neighboring ferrocenyl and the ferricenyl moiety. The high concentration is ascribed to high permeation and accumulation of the hydrophobic FcMA into the hydrophobic polystyrene particle.

The aqueous suspensions of the latex exhibited reversible voltammetric waves. The anodic and the cathodic peak currents were controlled by diffusion of the particles. Since D and n_{uv} are proportional to $a^{-1/2}$ and a^3, respectively, the diffusion-controlled current should be proportional to $a^{5/2}$. The observed power of a was 2.23 rather than 2.50. When

the size effect is expressed as n_{cv}/n_{uv}, the proportionality of n_{cv}/n_{uv} to $a^{-0.47}$ suggests the larger contribution of rotational diffusion to the current for larger particles.

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